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Efficient Calculation of Rovibrational Energy Levels of General Tetratomic Molecules

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Computational methods for the determination of bound rovibrational energy levels of tetratomic molecules are presented. The methods are designed for orthogonal internal coordinates in the body-fixed formulation. The discrete variable representation and sequential inclusion of the internal degrees of freedom are employed in combination with the successive diagonalization-truncation technique. This procedure allows the construction of the final full-dimensional Hamiltonian matrix of relatively modest size, which is diagonalized with the help of conventional dense matrix algorithms to give both rovibrational energies and wave functions. The characterization of the molecular energy levels calculated by the methods described here is done in an automatic fashion owing to the availability of the wave functions.

1 Introduction

Quantum mechanical investigations of the spectral and dynamical behavior of chemical systems are important for attaining a deeper theoretical understanding of chemistry at the molecular level. High accuracy quantum mechanical calculations over a wide range of molecular energies afford useful insights e.g. into the nature of anharmonicity and intermode coupling effects. Since all of the information that can be known about a quantum state are contained in the wave function, the determination of the eigenvectors (wave functions) simultaneously with the determination of the eigenvalues (energies) is essential for finding a reliable state/process characterization by the theoretical means. The decoding of the information carried by the wave function is a problem of great importance in physical chemistry.

Four-particle systems are a challenging computational task since several million basis functions may easily be required to achieve a good description of the internal vibrational motion. For improperly designed basis, the computation can easily suffer from basis set explosion. The rate determining steps in large-scale calculations for tetratomic molecules are the evaluation of a six-dimensional potential energy function and the diagonalization of the Hamiltonian matrix. While the kinetic energy matrix elements are readily evaluated analytically, the integrals over the six-dimensional potential energy are in general solved with help of numerical quadrature rules. The matrix diagonalization is performed either by means of a standard (Householder) algorithm in conjuction with numerical schemes for the construction of a very compact basis[1−5] or by employing a Lanczos algorithm in approaches favoring uncontructed primary basis set functions[6−8]. The eigenvalue calculation by means of methods based on a Lanczos algorithm requires no storage of the Hamiltonian matrix. The storage of Lanczos vectors is, however, necessary for the wave function determination.

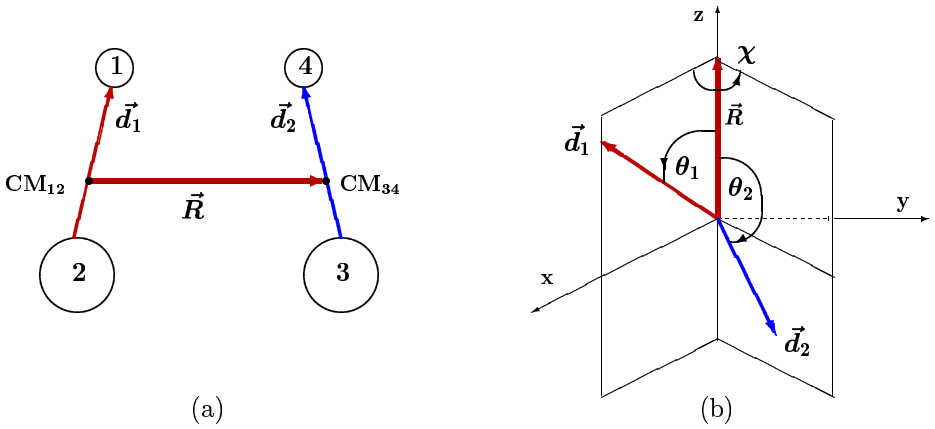

Figure 1. (a) Orthogonal vectors $\mathbf{R}, \mathbf{d}_1, \mathbf{d}_2$ of the (diatom-diatom) orthogonal description. The center of mass of the subunit ij is denoted by CM_{ij}. (b) Two vector body-fixed formulation for tetratomic molecules. The body-fixed $(\mathbf{R}, \mathbf{d}_1)$ reference frame is specified by aligning the body-fixed z axis with the vector $\mathbf{R}$ and by requiring that the vectors $\mathbf{R}, \mathbf{d}_1$ span the body-fixed (zx) plane. The origin of the frame is the molecular center of mass.

Highly efficient theoretical methods for the accurate quantum mechanical calculation of a large number of the bound rovibrational energy levels (eigenvalues and eigenvectors) of general tetratomic molecules are developed by the author[2−5]. The methods, termed DVR(+R)+FBR, DVR(+Rd)+FBR, DVR(6), and DVR(3)+DGB, employ the discrete variable representation of several vibrational coordinates in combination with the sequential diagonalization-truncation scheme and involve no dynamical approximation. Their unique feature is a very detailed eigenfunction analysis based on vibrationally averaged geometries and several adiabatic projection schemes for the automatic energy level characterization, which are carefully designed with the purpose of assigning approximate quantum numbers to exact quantum states. The energy level characterization approach based on the quantum state correlation scheme, which is recently developed for the DVR(6), is the first method treating this topic in a quantitative fashion[4].

The methods developed make use of the kinetic energy operator for orthogonal internal vectors in the body-fixed formulation (Sec. 2). The computational methodology is based on the discrete variable representation (Sec. 3). For the angular degrees of freedom, two basis sets are considered (Sec. 4) and their application for DVR based approaches is briefly described (Sec. 5).

2 Kinetic Energy Operator for Tetratomic Molecules

In the spherical polar parametrization, the internal geometry of a rotating tetratomic molecule described by three internal vectors $\mathbf{R}, \mathbf{d}_1, \mathbf{d}_2$ is given in terms of the three radial coordinates R, d_1, d_2, the two bending angles θ_1, θ_2, and the dihedral angle χ, as shown in Fig. 1. For an entirely orthogonal set of internal vectors, such as the (diatom-diatom)

vectors of Fig. 1(a), the body-fixed expression of the kinetic energy operator $\hat{T}$ attains the maximally separable form compactly written as[3]

$$\hat{T} = \hat{T}_{vib} + \hat{T}_{rot} + \hat{T}_{rv}, \tag{1}$$

where

$$\begin{aligned} 2\,\hat{T}_{vib} = {} & 2\,\hat{T}_{str}(R, d_1, d_2) + f(R, d_2)\,\hat{l}_2^2 \\ & - f(R, d_1)\,\left[\hbar^2\left(\frac{\partial^2}{\partial\theta_1^2} + \cot\theta_1\frac{\partial}{\partial\theta_1}\right) - \frac{1}{\sin^2\theta_1}\left(\hat{J}_z - \hat{l}_{2z}\right)^2\right], \end{aligned} \tag{2}$$

$$2\,\hat{T}_{rot} = \frac{1}{\mu_R R^2}\,\left[\hat{J}^2 - 2\,(\hat{J}_z - \hat{l}_{2z})^2\right], \tag{3}$$

$$\begin{aligned} \hat{T}_{vr} = \frac{1}{\mu_R R^2}\,\Big[& i\hbar\left(\hat{J}_y - \hat{l}_{2y}\right)\frac{\partial}{\partial\theta_1} + \cot\theta_1\,\left(\hat{J}_x - \hat{l}_{2x}\right)\left(\hat{J}_z - \hat{l}_{2z}\right) \\ & - \hat{J}_x\,\hat{l}_{2x} - \hat{J}_y\,\hat{l}_{2y} - \hat{J}_z\,\hat{l}_{2z}\Big]. \end{aligned} \tag{4}$$

In the latter expressions, $\hat{T}_{str}$ is the kinetic energy of the stretching vibrations and $\mu_R, \mu_{d_1}, \mu_{d_2}$ are the reduced masses associated with the radial coordinates R, d_1, d_2. The inverse of the reduced mass associated with the bending vibration is

$$f(R, d_i) = 1/\mu_R\,R^2 + 1/\mu_{d_i}\,d_i^2. \tag{5}$$

The vibrational angular momentum operator describing the orbiting of the vector $\mathbf{d}_2$ in the body-fixed $(\mathbf{R}, \mathbf{d}_1)$ frame of Fig. 1(b) is denoted by $\hat{\mathbf{l}}_2$ and $l_2 = l_2(\theta_2, \chi)$. The body-fixed projections of the total angular momentum operator $\hat{\mathbf{J}}$ are $\hat{J}_x, \hat{J}_y, \hat{J}_z$. The kinetic energy operator of Eq. (1) contains no radial-angular derivative cross terms. This feature is important for the construction of suitable potential adapted radial basis functions.

The compact expression of $\hat{T}$ from Eq. (1) is applicable to any set of three translationally and rotationally invariant orthogonal vectors used to describe the internal geometry of a tetratomic molecule. The reduced masses μ_R, μ_1, μ_{d_2} are the only vector specific parameters in Eq. (1). As shown before[3], μ_R, μ_1, μ_{d_2} are given by simple analytical forms and can easily be calculated for a chosen set of internal vectors. The uniqueness of $\hat{T}$ allows the application of a single computer program to different classes of four-particle systems. This feature is a distinct practical advantage important in variational energy level calculations.

3 Discrete Variable Representation

In the one-dimensional case, the Hamiltonian matrix elements H_{ij} in the orthogonal basis $\{\phi_i\}$ are given by

$$H_{ij} = \int \phi_i \hat{H} \phi_j\,dx = T_{ij} + V_{ij} = T_{ij} + \sum_z \mathcal{T}_{iz}\,V(x_z)\,\mathcal{T}_{jz}. \tag{6}$$

Here, the integrals over the potential energy V are solved numerically by employing the integration nodes x_z and the integration weights w_z, such that $\mathcal{T}_{iz}$ equals to $\sqrt{w_z}\phi_i(x_z)$. The representation of the Hamiltonian matrix in the ϕ-basis of the finite size N is known as the N-dimensional finite basis representation (FBR). For the numerical integration of Eq. (6) performed by means of the appropriate N-point quadrature rule, the N-dimensional

FBR is related by the $N \times N$ unitary FBR-DVR transformation matrix $\boldsymbol{\mathcal{T}}$=$\{\mathcal{T}_{iz}\}$ to the discrete variable representation (DVR) as follows

$$ {}^{(DVR)}\mathcal{H}_{z_1 z_2} = \sum_{i,j} \mathcal{T}_{iz}\ {}^{(FBR)}T_{ij}\ \mathcal{T}_{jz} \ + \ \delta_{z_1 z_2}\ {}^{(DVR)}V(x_z). \tag{7} $$

In the DVR, the potential energy matrix is diagonal with respect to the DVR points $\{x_z\}$.

As seen in Eq. (7), the integrals over V in the DVR become a number $V(x_z)$ giving a local value of V at the DVR point x_z. This is a distinct advantage of the DVR over the FBR counterpart important from the computational viewpoint. Since the DVR allows an efficient distribution of actual numerical work for the evaluation of V, DVR based methods are often preferable approaches for solving the Schrödinger equation due to their flexibility and easy implementation. Theoretical methods involving the discrete variable representation are originally introduced by Light[9,10]. The DVR has evolved into a standard approach for the quantum mechanical calculation of energy spectra of triatomic molecules[9,11,12].

The integration nodes and weights of Gauss quadrature rules are calculated by diagonalizing the Jacobi matrix constructed from the three-term recurrence relation[13]. The dual orthogonality of N DVR points is insured by the Christoffel-Darboux identity[14].

4 Angular Basis for Tetratomic Molecules

We consider two types of angular basis functions for tetratomic molecules. The parity-adapted angular basis functions, termed **Basis 1**, are of a non-direct product type and given for the total angular momentum **J** by[3]

$$ \begin{aligned} A^{Jp}_{Kkjl} &= N_{Kk}\ \overline{P}_j^{|k-K|}\ \left[\ Y_l^k\ |J,K,M\rangle + (-1)^{J+K+k+p}\ Y_l^{-k}\ |J,-K,M\rangle\ \right] \\ B^{Jp}_{Kkjl} &= N_{Kk}\ \overline{P}_j^{k+K}\ \left[\ Y_l^k\ |J,-K,M\rangle + (-1)^{J+K+k+p}\ Y_l^{-k}\ |J,K,M\rangle\ \right] \end{aligned} \tag{8} $$

where $Y_l^k = Y_l^k(\theta_2, \chi)$ are spherical harmonics, $\overline{P}_j^{k_j}$ normalized associated Legendre functions in $\cos\theta_1$, and $|J,K,M\rangle$ symmetric top eigenfunctions. The quantum numbers of the projection of **J** onto the Z-axis of the space-fixed and onto the z-axis of the body-fixed frame are M and K, respectively. The quantum number associated with $\hat{l}_{2z}$ is k. The basis functions of Eq. (8) allow easy analytical evaluation of the kinetic energy matrix elements and guarantee their finite size in spite of singular terms in Eq. (2) that are divergent as θ_i goes either to 0 or π.

Total angular momentum J, its space-fixed projection M, and parity p are strictly conserved quantum numbers for eigenstates of a tetratomic molecule, i.e. all Hamiltonian matrix elements are diagonal in J, M, and p. For the basis of Eq. (8), the kinetic energy matrix elements are also diagonal in j and l and nonzero for $\Delta K = \pm 1$ and $\Delta k = \pm 1$, such that the kinetic energy matrix is sparse after the angular integration[3]. The potential energy matrix in Basis 1 factors into two parity-adapted blocks. The matrix element of V

between e.g. the two B^{Jp}_{Kkjl} functions reads in the FBR as

$$V^{k_1 j_1 l_1}_{k_2 j_2 l_2}(R, d_1, d_2) = N_{Kk_1} N_{Kk_2} (-1)^{k_1+k_2} (1/\pi) \times \int_{-1}^{1}\int_{-1}^{1} \overline{P}^{k_1}_{l_1}(x_2)\, \overline{P}^{k_1+K}_{j_1}(x_1)\, \overline{P}^{k_2}_{l_2}(x_2)\, \overline{P}^{k_2+K}_{j_2}(x_1)\, dx_1\, dx_2 \times \int_0^{2\pi} \cos(k_2 - k_1)\chi\, d\chi\, V(R, d_1, d_2, \theta_1, \theta_2, \chi), \tag{9}$$

where $x_i = \cos\theta_i$. In the latter equation, the associated Legendre functions of different order are coupled due to the dependence of the potential energy on the torsional coordinate χ and the design of the DVR in connection with Basis 1 is not straightforward.

The parity-adapted angular basis of a direct product type, called **Basis 2**, is written for $J = 0$ as[4]

$$\overline{P}^{(\alpha_1,\beta_1)}_{n_1}(\cos\theta_1)\, \overline{P}^{(\alpha_2,\beta_2)}_{n_2}(\cos\theta_2)\, C_k(\chi), \tag{10}$$

where $\overline{P}^{(\alpha_i,\beta_i)}_{n_i}$ stands for orthonormalized Jacobi functions, whereas C_k denotes Chebyshev polynomials T_k of the first kind and Chebyshev functions U_k of the second kind used respectively for even-parity and odd-parity calculation. Since the order (α_i, β_i) of the Jacobi functions is decoupled from k in Eq. (10), Basis 2 is readily adapted for the DVR.

5 Computational Strategy

Several computational strategies are developed for tetratomic molecules. The DVR(+R)+FBR and DVR(+Rd)+FBR approaches employ Basis 1, whereas the DVR(6) and DVR(3)+DGB make use of Basis 2. All four methods employ a contraction scheme resulting from several diagonalization/truncation steps to construct a very compact and efficient basis set, in which the final matrix is of modest size and can be diagonalized by standard routines which, in addition to energies, provide wave functions in a simple fashion. Wave functions are indispensable for the calculation of various quantities, such as vibrationally averaged geometries, whose values are instructive for making quick preliminary quantum number assignments to the calculated states.

The fact that all off-diagonal matrix elements of the kinetic energy operator from Eq. (1) are attributed a single factor $1/2\mu_R R^2$ from the radial space is utilized in the DVR(+R)+FBR and DVR(+Rd)+FBR in conjunction with a pointwise representation of the radial coordinate R. The DVR(+R)+FBR and DVR(+Rd)+FBR methods are favorable for the computation of rovibrational ($J \neq 0$) energies of any tetratomic molecule and for the vibrational calculation for linear tetratomic molecules since Basis 1 avoids the possible singularities in the kinetic energy matrix. The DVR(6) and DVR(3)+DGB methodologies are advantageous for nonlinear tetratomic molecules since the discretization of the entire three-dimensional angular space allows a very efficient distribution of numerical work involving the evaluation of the six-dimensional potential energy function.

The computational methods described here are employed for the calculation of (ro)vibrational energies of several tetratomic molecules, like HOCO, $(HF)_2$, H_2O_2, H_2C_2, and H_2CO. The high efficiency and flexibility of our approaches have allowed the determination of various quantities, such as spectroscopic constants, dissociation energies, and the

number of bound states, as well as to study characteristic energy level patterns in various parts of the energy spectrum[2−5].

5.1 Computational Strategy for Basis 1

The DVR(+R)+FBR method makes use of combined discrete variable and finite basis representations of the angular coordinates $(\theta_1, \theta_2, \chi)$, a discretized Jacobi distance R, and eigenfunctions for (d_1, d_2) in conjunction with several diagonalization/truncation steps. The pointwise representation of the bending angles θ_1, θ_2 and the FBR for the torsional coordinate χ are introduced as the primary description in the (DVR+FBR) of the three-dimensional angular space $(\theta_1, \theta_2, \chi)$.

In the (DVR+FBR) of the two-dimensional space (θ, χ), the FBR-DVR transformation matrix $\mathcal{T}$ for θ is given by the following direct sum

$$\mathcal{T} \;=\; \sum_{m}^{\oplus} \mathcal{T}^m. \tag{11}$$

The elements of the submatrix $\mathcal{T}^m$ are

$$T^m_{lz_i} \;=\; \sqrt{\omega_{z_{i;m}}}\;\; \overline{P^m_l}(z_{i;m}), \tag{12}$$

where $z_{i;m}$=$\cos\theta_i$ and $\omega_{z_{i;m}}$ are the i-th DVR point and weight for Gauss-Legendre quadrature of order m. The matrix $\mathcal{T}$ is orthogonal and block diagonal in the (DVR+FBR). The similarity transformation by $\mathcal{T}$ changes the finite basis representation in the functional space spanned by Y^m_l to the combined (DVR+FBR) specified by $(m, z_{i;m})$. The (DVR+FBR) matrix element of $V = V(\theta, \chi)$ becomes

$$\begin{aligned}\langle z_{1;m_1} m_1 \mid V \mid z_{2;m_2} m_2\rangle &= \sum_{l_1,l_2} \mathcal{T}^{m_1}_{l_1 z_1}\; \langle l_1 m_1 \mid V \mid l_2 m_2\rangle\; \mathcal{T}^{m_2}_{l_2 z_2} \\ &\approx V^{m_1,m_2}(z_{1;m_1})\; \mathcal{R}^{z_1:m_1}_{z_2 m_2}\end{aligned} \tag{13}$$

when the θ-integration in the FBR is performed by Gauss-Legendre quadrature of order m selected such that $m = \min(m_1, m_2)$. The auxiliary matrix $\mathcal{R}$ is defined by

$$\mathcal{R}^{z_1:m_1}_{z_2 m_2} = \sum_{l_2=m_2} \mathcal{T}^{m_2}_{l_2 z_2}\; \sqrt{w_{z_{1;m_1}}}\;\; \overline{P}^{m_2}_{l_2}(z_{1;m_1}). \tag{14}$$

In Eq. (13), the integral over χ

$$V^{m_1,m_2}(;z_{1;m_1}) \;\sim\; \int_0^{2\pi} V(z_{1;m_1},\varphi)\; e^{i(m_2-m_1)\;\varphi}\; d\varphi \tag{15}$$

can be solved by means of Gauss-Chebyshev quadrature for each of the (m_1, m_2) pairs at the DVR θ-point $z_{1;m_1}$.

The potential energy DVR matrix element of Eq. (13) is diagonal in z only for $m_1 = m_2$. One may, however, note that a single evaluation of the potential energy at the point $z_{1;m_1}$ is required in Eq. (13) for the calculation of all matrix elements $\langle z_{1;m_1} m_1|V|z_{2;m_2} m_2\rangle$ with variable $z_{2;m_2}$. In actual calculation, the matrices $\mathcal{T}$ and $\mathcal{R}$ can be precomputed and retained for later use.

In the case of tetratomic molecules, the matrix element of the potential energy in the DVR comprised of the θ_1 grid points $a_{i;k}$ and θ_2 grid points $z_{j;k}$ can be calculated from

the corresponding FBR result of Eq. (9) by employing the transformation matrices $\mathcal{T}_1$ and $\mathcal{T}_2$ defined in analogy to Eq. (11). For $J = 0$, we obtain

$$V^{k_1 z_1 a_1 \alpha_1 \beta_1}_{k_2 z_2 a_2 \alpha_2 \beta_2} = N_{Kk_1} N_{Kk_2} (-1)^{k_1+k_2}\, \delta_{\alpha_1 \alpha_2}\, \mathcal{R}^{z_1 k_1}_{z_2 k_2}\, \mathcal{R}^{a_1 k_1}_{a_2 k_2}\, 2/M \times \sum_g \cos(k_2 - k_1)\chi_g \sum_{x_1, x_2} C^{\beta_1}_{x_1 x_2}\, C^{\beta_2}_{x_1 x_2}\, V(R_\alpha, x_1, x_2, a_{1;k_1}, z_{1;k_1}, \chi^g). \tag{16}$$

In the latter equation, the χ-integration is done by means of the M-point Gauss-Chebyshev quadrature involving the nodes χ_g. The expansion coefficients of the two-dimensional (d_1, d_2) eigenfunction in the discrete basis x_1, x_2 are denoted by $C^{\beta}_{x_1 x_2}$ in Eq.(16).

The discrete points R_α, x_1, x_2 used in Eq. (16) are obtained by diagonalizing the appropriate coordinate in an eigenfunction basis precomputed for a chosen reference potential. The matrix elements of $1/\mu_i d_i^2$ occurring in the reduced mass for the bending vibration, Eq. (5), are precomputed for the 2D (d_1, d_2) eigenfunctions and saved for later use.

The grid points (x_1, x_2) are employed as a primary basis for (d_1, d_2) in the DVR(+Rd)+FBR. The potential energy matrix element given by

$$V^{k_1 z_1 a_1 \alpha_1 x_1' x_2'}_{k_2 z_2 a_2 \alpha_2 x_1 x_2} = N_{Kk_1} N_{Kk_2} (-1)^{k_1+k_2}\, \delta_{\alpha_1 \alpha_2}\, \delta_{x_1' x_1}\, \delta_{x_2' x_2}\, \mathcal{R}^{z_1 k_1}_{z_2 k_2}\, \mathcal{R}^{a_1 k_1}_{a_2 k_2}\, 2/M \times \sum_g \cos(k_2 - k_1)\chi_g\, V(R_\alpha, x_1, x_2, a_{1;k_1}, z_{1;k_1}, \chi^g) \tag{17}$$

for the DVR(+Rd)+FBR are simpler than the corresponding expression from Eq. (16) for the DVR(+R)+FBR due to the elimination of the similarity transformation by the matrix C.

The performance of the DVR(+R)+FBR algorithm appears competitive with approaches based on the Lanczos method. Our calculation[2,3] for the vibrational levels of $(HF)_2$ and HOCO took respectively 15 CPU min and 9 CPU h on a CRAY T90 (single processor). Wu et al.[7] obtained the lowest 40 bound state energies and the associated wave functions for $(HF)_2$ in 10.5 CPU min on 126 processors of a CRAY T3E. The calculation by Lehoucq et al.[6] gave only the level energies of HOCO in 10.7 CPU h on 54 nodes of an IBM SP. The potential energy surface due to Quack and Suhm[15] is used for $(HF)_2$ and due to Schatz, Fitzcharls, and Harding[16] for HOCO.

5.2 Computational Strategy for Basis 2

The DVR(6) and DVR(3)+DGB methods make use of the discrete variable representation of the three angular coordinates in combination with Basis 2. The angular degrees of freedom are taken sequentially into account. After adding a new angular coordinate, the higher-dimensional Hamiltonian matrix is calculated and diagonalized. Truncation of the basis follows each diagonalization. The procedure of the DVR(6) and DVR(3)+DGB is schematically shown in Fig. 2. The grid points in θ_1, θ_2, χ are denoted by a, z, g, respectively.

The three radial degrees of freedom are treated simultaneously for each of the angular triples (a, z, g) in Step 1. The eigenvalue problems for the fixed-angle three-mode Hamiltonian for the stretching vibrations

$$\hat{T}_{str}(R, d_1, d_2) + V(R, d_1, d_2, \theta_1^a, \theta_2^z, \chi^g) \tag{18}$$

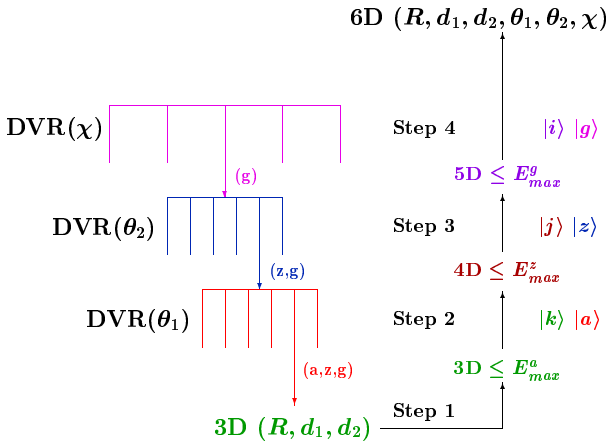

Figure 2. Computational strategy of the DVR(6) and DVR(3)+DGB methods.

are solved by employing 3D radial DVRs in the DVR(6) approach and real three-dimensional distributed Gaussian functions in the DVR(3)+DGB method. After solving the 3D radial eigenvalue problems, the primary radial basis is reduced by retaining only those 3D eigenvectors $|k\rangle$ of energy smaller than a preselected energy cutoff parameter E^a_{max}.

In Step 2, the bending coordinate θ_1 is coupled to the radial degrees of freedom. The 4D Hamiltonian matrices diagonal with respect to both z and g are computed for the basis $|k\rangle|a\rangle$. Having solved the 4D eigenvalue problems, the 4D basis is truncated by retaining only 4D eigenvectors $|j\rangle$ associated with the eigenvalues less than a predefined energy cutoff E^z_{max}. In Step 3, the 5D eigenvalue problems comprising the second bending coordinate θ_2 are formulated in the basis composed of $|j\rangle|z\rangle$. The number of the 5D eigenvectors $|i\rangle$ saved after the 5D diagonalizations is controlled by a preselected parameter E^g_{max}. The final 6D Hamiltonian matrix for all terms included is computed in the basis of $|i\rangle|g\rangle$ and diagonalized to give level energies and wave functions with the help of conventional algorithms for symmetric matrices.

The angular DVR in conjunction with sequential diagonalization/truncation procedure allows the development of schemes for automatic quantum number assignments for triatomic[11,12] and tetratomic[4,5] molecules. The strategy of the DVR(6) and DVR(3)+DGB methods readily permits adiabatic torsion approximation since the five-mode (stretch+bend) eigenenergies i, calculated at chosen torsional DVR points $\{g\}$ in Step 3 of Fig. 2, form effective (adiabatic) potentials ${}^{adi}V^i$ for the torsion. The effective potentials ${}^{adi}V^i$ are constructed by employing the quantum state character correlation scheme[4] and used to obtain torsional levels adiabatically separated from the stretch+bend motion. The determination of the adiabatic (zero-order) eigenvectors does not involve any new matrix element beyond those already evaluated. Automatic quantum number assignments to the calculated levels are obtained by locating the dominant zero-order contribution in the adiabatic expansions of the accurate full-dimensional wave functions. Adiabatic expansions of the numerically exact wave functions are obtained by simple matrix multi-

	H_2CO	H_2O_2	HOCO
(K, N_1, N_2)	$(8, 12, 12)$	$(14, 12, 12)$	$(14, 15, 35)$
$[M, M_1, M_2]$	[10,10,10]	[12,9,9]	$[14, 8, 6]$
E^a_{max} (cm^{-1})	23000	20000	3000
E^z_{max} (cm^{-1})	21500	20000	2000
E^g_{max} (cm^{-1})	20000	16000	-1000
N_{prim}	1 152 000	1 959 552	4 939 200
N_{final}	4 311	4 840	4 090
CPU (h)	2.0	3.8	7.9

Table 1. Numerical parameters employed for the DVR(6) calculation of the vibrational energy levels of H_2CO, H_2O_2, and HOCO. The number of the angular DVR $(\chi, \theta_2, \theta_1)$ points is denoted by (K, N_1, N_2), whereas $[M, M_1, M_2]$ stands for the number of the radial DVR points in $[R, d_1, d_2]$. The energy cutoff parameters E^a_{max}, E^z_{max}, and E^g_{max} are employed to truncate the primary basis set at different stages of the DVR(6) calculation. The size of the primary basis set and of the final 6D matrix are denoted by N_{prim} and N_{final}, respectively. The CPU times are given for a CRAY T90 (single processor).

plications. The adiabatic projection methods are used to study the intramolecular dynamics of H_2O_2[5] and HOCO, as well as for the investigation of local-mode vs normal-mode phenomena in the excited stretching states of H_2O_2 and H_2CO.

The integration and energy cutoff parameters used for the calculation of the vibrational energy levels of H_2CO, H_2O_2, and HOCO by means of the DVR(6) method are summarized in Table 1. The primary basis comprising 1 000 000-5 000 000 functions is reduced by $E^a_{max}, E^z_{max}, E^g_{max}$ to the size N_{final} of 4 000-5 000 for the final full-dimensional vibrational Hamiltonian matrix in Table 1. The CPU times given in Table 1 refer to the calculation of eigenenergies with eigenvectors and to the eigenfunction analysis for a large number of the calculated states. The potential energy surface of Carter, Handy, and Demaison[1] is employed for H_2CO, of Koput, Carter, and Handy[17] for H_2O_2, and of Schatz, Fitzcharls, and Harding[16] for HOCO.

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